Fully self-consistent GW calculations for atoms and molecules

Stan, A.; Dahlen, N.E.; van Leeuwen, R.

Published in:
Europhysics Letters

DOI:
10.1209/epl/i2006-10266-6

Publication date:
2006

EUROPHYSICS LETTERS

Europhys. Lett. (2006)
DOI: 10.1209/epl/i2006-10266-6

Fully self-consistent GW calculations for atoms and molecules

A. Stan, N. E. Dahlen and R. van Leeuwen

Rijksuniversiteit Groningen, Materials Science Centre, Theoretical Chemistry Nijenborgh 4, 9747AG Groningen, The Netherlands

received 11 April 2006; accepted in final form 29 August 2006
published online 20 September 2006

PACS. 71.15.-m – Methods of electronic structure calculations.
PACS. 31.15.Lc – Quasiparticle methods.

Abstract. – We solve the Dyson equation for atoms and diatomic molecules within the GW approximation, in order to elucidate the effects of self-consistency on the total energies and ionization potentials. We find GW to produce accurate energy differences although the self-consistent total energies differ significantly from the exact values. Total energies obtained from the Luttinger-Ward functional $E_{\rm LW}[G]$ with simple, approximate Green functions as input, are shown to be in excellent agreement with the self-consistent results. This demonstrates that the Luttinger-Ward functional is a reliable method for testing the merits of different self-energy approximations without the need to solve the Dyson equation self-consistently. Self-consistent GW ionization potentials are calculated from the Extended Koopmans Theorem, and shown to be in good agreement with the experimental results. We also find the self-consistent ionization potentials to be often better than the non-self-consistent G_0W_0 values. We conclude that GW calculations should be done self-consistently in order to obtain physically meaningful and unambiguous energy differences.

Introduction. – Green function methods have been used with great success to calculate a wide variety of properties of electronic systems, ranging from atoms and molecules to solids. One of the most successful and widespread methods has been the GW approximation (GWA) [1], which has produced excellent results for band gaps and spectral properties of solids [2,3], but so far has not been explored much for atoms and molecules, although it has been known that for atoms the core-valence interactions are described much more accurately by GW than Hartree-Fock (HF) [4]. Moreover, the GW calculations are rarely carried out in a self-consistent manner, and the effect of self-consistency is for this reason still a topic of considerable debate [5,6]. In this paper we present self-consistent all-electron GW (SC-GW) calculations for atoms and diatomic molecules. The reason for doing these calculations is twofold: Firstly, we want to study the importance of self-consistency within the GW scheme. Such calculations are usually avoided due to the rather large computational effort involved. It has been suggested that self-consistency will in fact worsen the spectral properties, though calculations on silicon and germanium crystals indicate that this is not always the case [5]. The second reason is that we aim to study transport through large molecules and molecular chains, where it is essential to account for the screening of the long range of the Coulomb interaction. The calculations on diatomic molecules are the first step in this direction.

The GWA is obtained by replacing the bare Coulomb interaction v in the exchange self-energy with the dynamically screened interaction W, such that $\Sigma = -GW$. The screened interaction also depends on the Green function, and one thus needs to solve a set of coupled equations for G and W. One usually goes through only a single iteration of this scheme. With an initial Green function G_0 calculated from, *e.g.*, the local density approximation (LDA), one calculates W and Σ, and subsequently obtains a new Green function from the Dyson equation. This scheme, known as the G_0W_0 approximation, has produced good results for a wide variety of systems [2], but suffers from a dependence on the choice of the initial G_0. Moreover, observables like the total energy are not unambiguously defined, and can be calculated in several different ways. These problems can be cured by performing self-consistent calculations [7], since the GWA is a Φ-derivable approximation (see fig. 1). The fact that self-consistency removes these ambiguities does not imply that the results are necessarily closer to the exact values. For the electron gas it was shown that self-consistency actually worsens the spectral properties, while the total energy is in excellent agreement with Monte Carlo results [8]. On the other hand, for a system of very localized interactions, SC-GW produced poor results for both total energies and spectral properties [9]. Furthermore, Delaney *et al.* [6] recently published SC-GW results for the ionization potential of the Be atom that were worse than those of G_0W_0. Calculations on the Si and Ge crystals have, however, shown that self-consistency leads to improved band gaps [5].

General formulation. – In this paper, we study the importance of self-consistency in GW for atoms and diatomic molecules. We compare the self-consistent total energies to those obtained from the Luttinger-Ward (LW) functional [10] which was earlier used to estimate the GW total energy for atoms [11] and the electron gas [12]. The LW functional $E_{\rm LW}[G]$ is a variational energy functional in the sense that $\delta E_{\rm LW}[G]/\delta G = 0$, when G is a self-consistent solution of the Dyson equation. This variational property suggests that evaluating $E_{\rm LW}$ on an approximate Green function obtained from, *e.g.*, HF or LDA calculations will give a result very close to the self-consistent value. This was earlier shown to be the case for the second-order self-energy [13], and investigating the stability of the LW functional also for the GWA is an important goal of this paper. The previously published LW calculations [11] indicated that the GW total energies are not very accurate, but the essential question is rather whether total energy differences are produced accurately. We have for this reason also calculated the binding curve of the H_2 molecule and two-electron removal energies $\Delta E = E_{N-2} - E_N$.

We use the finite-temperature formalism, with a temperature T (we are only considering the limit $T \to 0$) and a chemical potential μ. The Green function depends on the imaginary time coordinate τ, in the range $-\beta \leq \tau \leq \beta \equiv 1/k_BT$, where k_B is the Boltzmann constant. It satisfies the Dyson equation

$$\left[-\partial_\tau + \frac{\nabla^2}{2} - w(\boldsymbol{r}) - v_H(\boldsymbol{r}) + \mu \right] G(\boldsymbol{x}, \boldsymbol{x}'; \tau) =$$

$$= \delta(\tau)\delta(\boldsymbol{x} - \boldsymbol{x}') + \int_0^\beta \mathrm{d}\tau_1 \int \mathrm{d}\boldsymbol{x}_1 \Sigma[G](\boldsymbol{x}, \boldsymbol{x}_1; \tau - \tau_1) G(\boldsymbol{x}_1, \boldsymbol{x}'; \tau_1), \tag{1}$$

where $\boldsymbol{x} = (\boldsymbol{r}, \sigma)$ denotes the space- and spin coordinates, $w(\boldsymbol{r})$ is the external potential, $\Sigma[G](\boldsymbol{x}, \boldsymbol{x}'; \tau)$ is the self-energy and $v_H(\boldsymbol{r})$ is the Hartree potential. The last two objects are functionals of the Green function, and the Dyson equation should therefore be solved self-consistently, together with the boundary conditions $G(\boldsymbol{x}, \boldsymbol{x}', \tau - \beta) = -G(\boldsymbol{x}, \boldsymbol{x}'; \tau)$ and $G(\boldsymbol{x}, \boldsymbol{x}'; 0^+) - G(\boldsymbol{x}, \boldsymbol{x}'; 0^-) = -\delta(\boldsymbol{x} - \boldsymbol{x}')$.

In the GWA (fig. 1) the electronic self-energy is given by $\Sigma = -GW$ using the screened

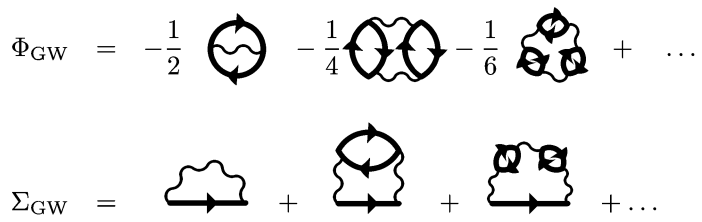

Fig. 1 – The GW self-energy Σ is the functional derivative of a functional $\Phi[G]$.

interaction $W = v + vPW$, where v is the bare Coulomb interaction $1/|\boldsymbol{r} - \boldsymbol{r}'|$ and $P = GG$ is the polarizability [1]. The Green function is transformed into a τ-dependent matrix by expanding it in a basis of molecular orbitals obtained from an initial HF calculation. These molecular orbitals are linear combinations of Slater functions located on the atomic centers [14]. The Green function, the $\Sigma[G]$ and the W are peaked around the endpoints ($\tau = 0$ and $\tau = \pm\beta$) [5, 13] so their representation on an even-spaced grid is inconvenient. Instead, we used a mesh which is dense around the end points [5].

Since we calculate the Green function on the imaginary time axis, it is inconvenient to calculate the ionization potentials by finding the poles of the Green function in frequency space, $G(\omega)$. We have instead used the extended Koopmans theorem (EKT) [15] where the ionization potentials are found from the eigenvalue equation

$$\sum_{ij} \Delta_{ij} u_j^m = -\lambda_m \sum_j \rho_{ij} u_j^m, \tag{2}$$

where $\Delta_{ij} = -\partial_\tau G_{ij}(\tau)|_{\tau=0^-}$, the density matrix is given by $\rho_{ij} = G_{ij}(0^-)$ and the matrix indices refer to the molecular orbital basis [13]. The eigenvalues λ_m are interpreted as $\lambda_m = E_m^{N-1} - E_0^N + \mu$, *i.e.* the ionization potentials plus the chemical potential. The EKT is known to be exact for the lowest ionization energies, if the exact Δ and ρ matrices are given [16]. For the HF approximation, the EKT eigenvalues obviously agree with the poles of the HF Green function, and it is an unproven conjecture that these two methods will give the same value for the first ionization potential when the Green function is calculated self-consistently within a conserving approximation. The EKT has recently been used to calculate ionization potentials for atoms and molecules from a self-consistent Green function using the second-order diagrams [13].

To calculate the SC-GW total energy $E = T + V_{ne} + U_0 + U_{\mathrm{xc}}$, we use the fact that the exchange-correlation part of the interaction energy is given by

$$U_{\mathrm{xc}} = \frac{1}{2} \sum_{ij} \int_0^\beta \mathrm{d}\tau \Sigma_{ij}(-\tau) G_{ji}(\tau), \tag{3}$$

and the kinetic energy T, nuclear-electron attraction energy V_{ne} and Hartree energy U_0 are trivially obtained from the density matrix ρ. There are many other ways to calculate the total energy from a given Green function, but only for a self-consistent solution of the Dyson equation will these methods give the same result [7]. One alternative is to calculate the energy from variational functionals of the Green function. LW have shown [10] that the total energy can be written as

$$E_{\mathrm{LW}}[G] = \Phi[G] - U_0 - \mathrm{Tr}\big\{\Sigma G\big\} - \mathrm{Tr}\ln[\Sigma - \mathrm{G}_{\mathrm{H}}^{-1}] + \mu \mathrm{N}, \tag{4}$$

TABLE I – *Total energies (in hartrees) calculated from SC-GW compared to CI values and results from the LW functional and Galitskii-Migdal formula evaluated on* G_{HF}.

System	E_{SC}^{GW}	$E_{\mathrm{LW}}^{GW}[G_{\mathrm{HF}}]$	$E_{\mathrm{GM}}[G_{\mathrm{HF}}]$	CI
He	−2.9278	−2.9277	−2.9354	$-2.9037^{(a)}$
Be	−14.7024	−14.7017	−14.7405	$-14.6674^{(a)}$
Be^{2+}	−13.6885	−13.6885	−13.6929	$-13.6556^{(a)}$
Ne	−129.0499	−129.0492	−129.0885	$-128.9376^{(a)}$
Mg	−200.1762	−200.1752	−200.2924	$-200.053^{(a)}$
Mg^{2+}	−199.3457	−199.3453	−199.3785	$-199.2204^{(a)}$
H_2	−1.1887	−1.1888	−1.1985	$-1.133^{(b)}$
LiH	−8.0995	−8.0997	−8.1113	$-8.040^{(c)}$

$^{(a)}$From ref. [17]. $^{(b)}$From ref. [18]. $^{(c)}$From ref. [19].

where G_H is the Hartree Green function, and $\Sigma = \delta\Phi/\delta G$. The trace indicates an integration over the spatial coordinates and τ [11], see also eq. (3). It is easily verified that $\delta E_{\mathrm{LW}}/\delta G = 0$ when G is a self-consistent solution of the Dyson equation (1). Hence, if we evaluate the LW functional on a simple input Green function, we obtain a result close to the self-consistent energy, since we make an error only to second order in the deviation from the self-consistent G. This means that we have a computationally cheap way of obtaining self-consistent total energies. The quality of the energies will ultimately be determined by the chosen self-energy approximation.

Within a molecular orbital basis, the Dyson equation (1) becomes a matrix equation. We introduce a reference Green function G_0 in order to write the equation on integral form,

$$G_{ij}(\tau) \;=\; \delta_{ij}G_{0,i}(\tau) + \int_0^\beta \mathrm{d}\tau_1 \int_0^\beta \mathrm{d}\tau_2 \sum_k G_{0,i}(\tau-\tau_1)\tilde{\Sigma}_{ik}(\tau_1-\tau_2)G_{kj}(\tau_2), \qquad (5)$$

where $\tilde{\Sigma} = \Sigma[G] - \Sigma_0$, and Σ_0 is the self-energy corresponding to G_0 [13]. We take G_0 and Σ_0 to be the HF Green function and self-energy, but this choice is arbitrary. Using, *e.g.*, LDA instead would not change any of the results. The inverse temperature is chosen to have a sufficiently large value, typically larger than 100 a.u. The value of the chemical potential is somewhat arbitrary, but should be in the gap between the highest occupied and the lowest unoccupied orbital. We checked that the observables calculated from the resulting Green function did not depend on the choice of β and μ. The calculations on the molecules were done at the experimental bond lengths.

Results. – In table I we show the SC-*GW* total energies of some atoms and small molecules. We have also included the $E_{\mathrm{LW}}[G_{\mathrm{HF}}]$ results, which are in spectacular agreement with the SC-*GW* values. This agreement is independent of the chosen basis set, and was earlier observed also for the second-order diagrams [13]. The third column shows the total energy calculated from G_{HF} using the Galitskii-Migdal [20] formula. In contrast to the LW results, these are not in good agreement with the self-consistent energies. This clearly demonstrates that different total energy functionals will not produce the same results when evaluated on a non-self-consistent Green function (in this case, G_{HF}), and it also demonstrates the importance of using the variational functionals for obtaining a result in agreement with the self-consistent values.

As a further test of the total energy functionals, we have calculated the total energy of the H_2 molecule for a range of internuclear separations. Figure 2 shows the SC-*GW* results

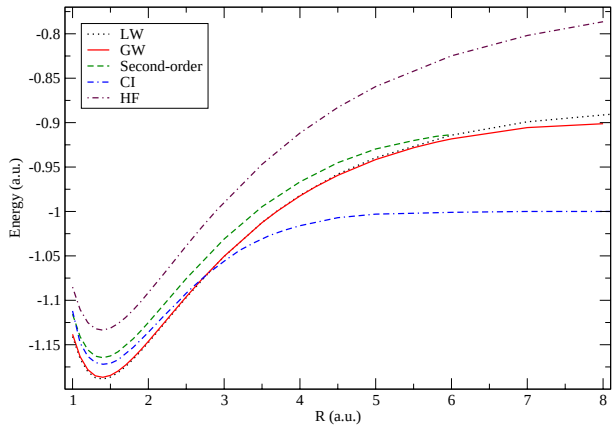

Fig. 2 – The total energy of the H_2 molecule, as a function of the interatomic distance, calculated within the second order, the self-consistent GWA, the $E_{\rm LW}^{GW}[G_{\rm HF}]$ functional and CI (from ref. [18]). For comparison, the HF results are also presented.

together with the $E_{\rm LW}[G_{\rm HF}]$ energy. The curves agree closely up to $R \approx 5$ a.u., and the deviation remains small even at $R = 8$. The gradual increase in the deviation is due to the fact that the input $G_{\rm HF}$ differs increasingly from the self-consistent Green function at large separations, making the variational property of $E_{\rm LW}$ less reliable. We also plotted benchmark configuration-interaction (CI) results and the binding curve obtained from the self-consistent Green function within the second-order self-energy approximation [13], which we were able to calculate up to $R = 6$. The second-order results are closer to the exact results than the GW curve around the equilibrium distance. This was to be expected, since the main feature of GWA is to screen the long-range interactions. For atoms or small molecules it is more important to take both direct and exchange diagrams into account to the same order. Also for the atoms, the SC-GW results are not particularly close to the CI results, as seen in table I. It should be noticed, however, that the shapes of the GW and the second-order curves are similar to each other and to the CI curve around the equilibrium bond distance. We finally note that, like the HF method, self-consistent GW is not a size-consistent method, *i.e.* the total energy calculated at large separations will not converge to the sum of the total energy of the fragments. This is not surprising, since the GWA is similar to HF in that the bare interaction in the exchange self-energy is replaced by a screened interaction and this screening is not sufficient to alleviate the deficiency of HF. This is an obvious problem when calculating molecular binding energies, and has been discussed in more detail in ref. [21].

Let us now turn to calculations of atomic energy differences. It is evident from the shape of the binding curves around the equilibrium separation in fig. 2, that SC-GW can produce accurate total energy differences. Calculations on atoms using the LW functional have also shown that two-electron removal energies, $\Delta E = E_{N-2} - E_N$, can be very accurately given within the GW approximation [11]. We therefore calculated the SC-GW removal energies of Be and Mg, as shown in table II. We find excellent agreement with the experimental results for both Mg and Be, the deviation being ten times smaller than those from the HF calculations. This improvement is in keeping with the results obtained by Shirley and Martin for G_0W_0 calculations on atoms [4]. In table III, we show the ionization potentials obtained from the EKT, both from the SC-GW and the non-self-consistent G_0W_0 Green function. The latter is obtained by iterating the Dyson equation once, starting from an LDA or HF Green function.

TABLE II – *Two-electron removal energies $E_{N-2} - E_N$ (in* eV*) calculated from SC-GW, compared to HF values and the experimental values.*

System	SC-GW	HF	Expt.[(a)]
Mg-Mg^{2+}	22.59	21.33	22.68
Be-Be^{2+}	27.59	26.17	27.53

[(a)]From ref. [22].

For most of the systems, the SC-GW ionization potentials are in good agreement with the experimental values, and in several cases better than those of G_0W_0. This is in contrast to the results for the electron gas, where self-consistency worsens the spectral properties [8].

The results for beryllium differ from those recently published by Delaney *et al.* [6]. We find a smaller difference between the SC-GW and the G_0W_0(LDA) results, and the latter value is also further away from the exact value than reported in ref. [6]. One explanation for this deviation may be that while we obtained the ionization potentials from the EKT, Delaney *et al.* calculated them from the poles of the Fourier-transformed function $G(\omega)$. For the self-consistent ionization potentials, these methods should give the same result (they do in fact only differ by 0.2 eV), but for the G_0W_0 Green function it is not obvious that the results should agree. Another difference is that we have carried out our calculations in a basis of Slater functions, while the orbitals in ref. [6] are represented on a grid. The Slater basis was systematically extended until reaching convergence with respect to the total energy. We include HF orbitals with very large eigenenergies, *e.g.*, for Be states up to 843 Hartree, while for Ne the highest orbital energy was 976 Hartree. We found good agreement between second-order Møller-Plesset calculations with our basis sets and highly converged results from the literature [23]. This does not imply simultaneous convergence of other properties such as the ionization potential. In table IV, we illustrate the convergence of the beryllium atom for two different basis sets. The main difference between the sets is that basis I contains Slater functions optimized for HF calculations [24]. The uncertainty of ~ 0.02 eV in the ionization potential indicated in table IV is typical for the calculations on atoms presented in table III.

Conclusions. – In summary, we have solved the Dyson equation within GWA to self-consistency for a number of atoms and diatomic molecules. We have shown that SC-GW gives good total energy differences and ionization potentials, significantly improving the HF results. We demonstrated that self-consistency improves the G_0W_0 ionization potentials for most systems studied and has the additional advantage of providing unambiguous results.

TABLE III – *Ionization potentials (*eV*) calculated from the EKT, using the self-consistent Green function and the Green function calculated from one iteration of the Dyson equation, starting from G_{LDA} and G_{HF}.*

System	G_0W_0 (LDA)	G_0W_0 (HF)	GW	Expt.[(a)]
He	23.65	24.75	24.56	24.59
Be	8.88[(b)]	9.19	8.66[(b)]	9.32
Ne	21.06	21.91	21.77	21.56
Mg	7.52	7.69	7.28	7.65
H_2	15.92	16.52	16.22	15.43
LiH	6.87	8.19	7.85	7.9

[(a)]From ref. [22].
[(b)]To be compared with the G_0W_0 value 9.25 and the SC-GW value 8.47, reported in in ref. [6].

TABLE IV – *Convergence of the beryllium ionization potential, IP, (in* eV*) and total energy (in hartrees) for two different basis sets. The value of l_{max} indicates the maximum angular momentum quantum number used in the basis.*

	$l_{\max}=2$	$l_{\max}=3$	$l_{\max}=4$	$l_{\max}=5$	$l_{\max}=6$	$l_{\max}=7$
IP: basis I	8.552	8.602	8.625	8.636	8.641	8.644
IP: basis II	8.439	8.615	8.637	8.649	8.654	8.656
E: basis I	−14.6954	−14.6999	−14.7016	−14.7024	−14.7028	−14.7028
E: basis II	−14.6807	−14.6998	−14.7015	−14.7024	−14.7027	−14.7028

Moreover, we have shown that the LW functional gives total energies in excellent agreement with the SC-*GW* energies, at a fraction of the computing time. This demonstrates the considerable usefulness of the LW functional for estimating the accuracy of various self-energy approximations.

* * *

We would like to thank U. VON BARTH for useful discussions.

REFERENCES

[1] HEDIN L., *Phys. Rev.*, **139** (1965) A796.
[2] ARYASETIAWAN F. and GUNNARSSON O., *Rep. Prog. Phys.*, **61** (1998) 237.
[3] GODBY R. W., SCHLÜTER M. and SHAM L. J., *Phys. Rev. B*, **37** (1988) 10159.
[4] SHIRLEY E. L. and MARTIN R. M., *Phys. Rev. B*, **47** (1993) 15404.
[5] KU W. and EGUILUZ A. G., *Phys. Rev. Lett.*, **89** (2002) 126401.
[6] DELANEY K., GARCÍA-GONZÁLEZ P., RUBIO A., RINKE P. and GODBY R. W., *Phys. Rev. Lett.*, **93** (2004) 249701.
[7] BAYM G., *Phys. Rev.*, **93** (1962) 1391.
[8] HOLM B. and VON BARTH U., *Phys. Rev. B*, **57** (1998) 2108.
[9] SCHINDLMAYR A., POLLEHN T. J. and GODBY R. W., *Phys. Rev. B*, **58** (1998) 12684.
[10] LUTTINGER J. M. and WARD J. C., *Phys. Rev.*, **118** (1960) 1417.
[11] DAHLEN N. E. and VON BARTH U., *Phys. Rev. B.*, **69** (2004) 195102.
[12] ALMBLADH C.-O., VON BARTH U. and VAN LEEUWEN R., *Int. J. Mod. Phys. B*, **13** (1999) 535.
[13] DAHLEN N. E. and VAN LEEUWEN R., *J. Chem. Phys.*, **122** (2005) 164102.
[14] Details on the basis sets are available upon request.
[15] SMITH D. W. and DAY O. W., *J. Chem. Phys.*, **62** (1975) 113.
[16] KATRIEL J. and DAVIDSON E. R., *Proc. Natl. Acad. Sci., USA*, **77** (1980) 4403.
[17] CHAKRAVORTY S. J., GWALTNEY S. R., DAVIDSON E. R., PARPIA F. A. and FISCHER C. F., *Phys. Rev. A*, **47** (1993) 3649.
[18] VAN LEEUWEN R., PhD Thesis (Vrije Universiteit, Amsterdam) 1994.
[19] LI X. and PALDUS J., *J. Chem. Phys.*, **118** (2003) 2470.
[20] GALITSKII V. M. and MIGDAL A. B., *Sov. Phys. JETP*, **7** (1958) 96.
[21] DAHLEN N. E., VAN LEEUWEN R. and VON BARTH U., *Phys. Rev. A*, **73** (2006) 012511.
[22] LIAS S. G., LEVIN R. D. and KAFAFI S. A., *Ion Energetics Data in NIST Chemistry WebBook, NIST Standard Reference Database Number*, Vol. **69**, edited by LINSTROM P. J. and MALLARD W. G. (National Institute of Standards and Technology, Gaithersburg MD, 20899 USA (`http://webbook.nist.gov`)) 2003.
[23] TERMATH V., KLOPPER W. and KUTZELNIGG W., *J. Chem. Phys.*, **94** (1990) 96.
[24] CLEMENTI E., *IMB J. Res. Develop. Suppl.*, **9** (1965) 2.